

November 14, 2004  
The Boeing Company

Ms Cheri Peele  
Washington Department of Ecology  
Lacey, WA.

Dear Ms Peele:

The Boeing Company provides the following comments on the Draft PBDE Chemical Action Plan as posted on the [flameretardant.org](http://flameretardant.org) website as of November 7, 2004. We appreciate that the Department agreed to a stakeholder committee to review the issues surrounding these three chemical formulations. Our involvement in the PBDE Chemical Action Plan stakeholder process has been very beneficial. We are in concurrence with comments provided by the Bromine Chemistry Council and the Association of Washington Businesses on issues not specifically addressed in this letter.

Our detailed review of the proposed PBDE Chemical Action plan identifies a overriding single fatal flaw- a lack of any meaningful risk or impact assessment to support the majority of recommendations. The DOE/DOH (the Agencies) urgency in completing the CAP in the time allotted under the Governor's executive order appears to underlie this failure to provide sufficient analysis of the complex range of technical, social, economic and health issues. A reasoned approach to a risk analysis may have addressed a number of contentious issues that are created with this CAP's recommendations. Hence, instead of identifying actions promote cooperation among the parties involved, this plan creates a divisive formula for future debate and dissention. A plans that is therefore unlikely to be effective in addressing the issues of concern.

Lacking a meaningful risk analysis, the agencies have substituted an extraordinary interpretation of the precautionary principle. The Agencies dependence on a derivative threat from deca-BDE (debromination) is hard to both understand and substantiate. The need for substantially greater research on debromination is documented in the reports from multiple governments. These same governments do not recommend a need to take any specific action, such as a ban, which the Agencies are recommending

A companion flaw is the lack of a systems-thinking approach to the question of economic or social impact. These analyses are as critically important in identifying the likely outcome of any Agency recommendation. This impact analysis is particularly important when considering the impact of a ban on a life saving chemical such as fire retardants. The agency's lack of analysis leaves unanswered questions about any increased risks of deaths and injuries in fires, the likelihood of more fires, and the environmental and health effects of combustion products in such fires. For example, the Agencies must determine that reducing the alleged risk by PBDE is greater than the impact of increasing the risk of death by fire. The Agencies must also establish the environmental effects of the additional burn products created by an increase in previously preventable fires further, the environmental and health effects of the alternative

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materials are, if anything, less understood than those of the PBDE family. Weighing the risks associated with a ban, the Precautionary Principle would lead one to take no action at this time. Rather, the prudent course of action is to monitor research on deca-BDE and the proposed substitutes so that fire protection is not compromised and environmental and health impacts are minimized.

The economics of the PBDE issue are being underplayed and unanalyzed in this CAP. The Agency's proposals will create one of a kind restriction in Washington State ranging from manufacture buy-back programs to a ban on electronics containing Deca-BDE. Each of these independent actions has a potential for multiple incidental impacts; any or all of which could lead to adverse economic conditions. In the above comment we considered the relative impact on fire safety. We now suggest that the Agencies must look seriously at what will happen to people subject to economic dislocation due to a non-competitive economic sectors resulting from these restrictions.

The multiple, complex and unresolved issue in the PBDE debate reinforce our concern that the Agencies have not had adequate time or resources to work through the myriad issues at play. A remedy to this situation is necessary by taking the following recommend actions:

- The Chemical Acton Plan be rescinded and reissued on a chemical specific basis (effectively two plans).
- Each CAP includes substantive risk and impact analysis.
- Coordinate with the US EPA as to action necessary, including a gap analysis specific to Washington State.
- The WDOE monitor deca-BDE science for emerging trends related to debromination.

Additional specific comments and recommendations are in the attachments.

Please contact the undersigned if you have question about our comments.

Sincerely,

Kirk Thomson  
Director- Boeing Environmental Affairs  
PO Box 3707 MC 7A-UU  
Seattle, WA 98124  
206-930-6122

### **1) The Chemical Action Plan Lacks Clarity.**

Comment: The plan is an incomprehensible mixture of discussions and information on three versions of the PBDE, Octa, Penta, and Deca. Two of these, Octa and Penta, materials have some showing of toxicity and are already being phased out of production by their manufacture. The EPA has taken action through TSCA to prevent their reintroduction into the country. The European Union (EU) has an effective ban on their use under its various rules. Deca-BDE has significantly different properties and regulatory environment than Oct/Penta-BDE. For any Washington Citizen to understand the varying effects between Octa /Penta and Deca requires clear independent presentation with science and technical facts specific to these substances. This report fails in this regard.

Recommendation: Rescind the current draft PBDE chemical action plan. Reissue the plan addressing each of the PBDE's under evaluation. Limit factual information to that which can be specifically correlated to the PBDE formulation under discussion in the plan. Where pertinent cross references between formulations are appropriate be sure that they are clearly identified. In interest of economy it may be feasible to combine the CAP for Octa and Penta –BDE since both are out of production and the challenges will be similarly focused on recycling issues. Deca-BDE however; is considerably different in effects and underlying knowledge. It must be discussed independently of the Oct and Penta versions.

## 2) Imprecise language adding to confusion:

Comment: The plan as written contains a number of statements that could be confusing to the public and policy makers as to whether the statement was speculation, unsubstantiated extrapolation or assumptions not in fact. The number of these statements occurring creates an inaccurate understanding of the impact of the chemicals under discussion. When combined with the interweaving of discussion of the various chemicals, as noted in attachment 1, it becomes impossible to discern if the discussion is fact, concept, extrapolation or guesswork. Some random example statements taken from the plan are:

- Page 55: In anticipation of the phase-out of Penta-BDE and Octa-BDE, **it is expected** that manufacturers are moving away from these products and identifying alternatives. In addition, a number of electronics manufacturers have been identified that are phasing out of all PBDEs, including Deca-BDE.  
Comment: Expected by who? What evidence do we have that the thousands of manufactures across the world are changing formulations. Was it market forces or better alternatives? What happens if EU does not ban deca-BDE, will manufactures return to this material? What are the net impact of the substitutes on the environment- is the life cycle cost of smelted metal cases greater or less than deca-BDE?
- Page 33: As reductive debromination has been observed in experiments using water with dissolved humic substances, **it must be assumed that this may also occur** in the environment. Other factors, not yet explored, may also influence both photolytic degradation rate and products.  
Comment: Policy decisions can not be based on Agency staff's assumptions. This statement creates an unfounded concern about degradation products.
- Page 27: Butt et al. found indoor levels of PBDEs in Southern Ontario were 1.5 to 20 times greater than outdoor levels on a site-by site basis. **They suggest** that indoor air may serve as a significant source of PBDEs to outdoor air. "  
Comment: Suggest" has no place in a document alleged to be filled with facts- it either is, or is to be confirmed (and hence is not).
- Page 27: **If** brominated dioxins and furans were present in substantial quantities, this could be a pathway for release to the environment.  
Comment: If? The word itself is the essence of speculation. It has no place in a policy document based on scientific analysis.
- Page 56: PBDEs are found in a **vast number** of consumer products, with **vast potential** for continued human exposure.  
Comment: "Vast" is a very hard term to quantify in a meaningful manner.

Such a term is more appropriate to description in tourist advertisements than use in a government policy document.

- Page iv: Each additional year that PBDE products are produced and sold will extend that timetable – and any related costs – **by a decade or more.**

Comment: Where in the literature is the data to support this statement. A statement designed more to create apprehension and a rush to judgment than understanding of chemical degradation processes, such as half-life.

One further example of inherent failure in the impartiality in this entire PBDE process is the public hearing announcement created and issued by the Agencies with full management approval, and at \$20,000 in cost. The advertisement, well known to the department, used language and baby photo that created a fear filled environment at the public hearing. It is this disturbing trend, the advertisement and the CAP language, that fuels a concern that a full and honest evaluation of the PBDE issue may not be possible within the Agencies. Concern that even makes the use of an “.org” website a matter that deserves questioning- not to mention the use of a photo of mother and child- creating an adverse implication for PBDE.

Recommendation: The extent to which imprecise language can be found suggests a need for an independent technical editor. An editor well versed in neutral, factual technical writing may be able to restructure and rewrite the recommended new documents to standards of impartiality & scientific clarity expected from a government agency. This rewrite will provide the policy makers and the public with a factually accurate view of the topic on which to determine actions.

Further, Agency executive management needs to reiterate to its staff that personal perspective on PBDE will not be allowed to influence developing Agency policy. This should include careful over-site of staff actions in all areas affecting CAP content and public notices.

Attachment 3:

**National and/or International actions and findings**

Comment: Action by Washington State on any of the PBDEs needs to be considered as a whole, not selectively, when compared to actions and findings by other government agencies.

- **National Academy of Science:** As noted in the CAP the National Academy of Sciences (NAS). NAS reviewed the toxicological and exposure data of 16 flame retardants, including Deca-BDE, to assess potential health risk to consumers and the general population resulting from potential exposure from the chemicals in residential furniture. Despite the lack of a complete database, the report concluded that Deca-BDE, along with a number of other flame retardants listed in Table 8, could be used on furniture with minimal risk, even under worst-case assumptions. (underlined for clarity)
- **State of California:** It is no surprise that when California considered the issue of banning PBDEs it sought expert evaluation resulting in a California legislatively mandated report:
  - “As required by AB 302, in June 2004 the Senate Office of Research submitted a report entitled “Polybrominated Diphenyl Ethers (PBDEs): Potential Hazards from DecaBDE and Unresolved Issues from AB 302” to the President Pro Tempore of the Senate and the Senate Environmental Quality Committee. The report stated that, based on the “likely potential harm to humans posed by decaBDE and the known human exposures to this chemical, it does not appear that human exposure to decaBDE is occurring at a level that is likely to be unsafe for human health or development.” **The report concluded that, at this time, it would be premature to add Deca-BDE** to the list of banned PBDEs contained in AB 302.<sup>181</sup>
- Even the EU, in a somewhat confusing analysis, has determined that there is insufficient information or harm to ban the use of Deca-BDE. EU staff responded to a WDOE request that: “The Conclusion is that further information and testing are required in an attempt to demonstrate whether the substance is or is not a safe product. Hence, Deca-BDE is currently being evaluated by the European Commission for exemption from the ban under the RoHS Directive. Through July 5, 2004, the Commission solicited written stakeholder comments in response to the following questions with regard to Deca-BDE:
  - Do feasible substitutes currently exist in an industrial and/or commercial scale?
  - Do any restrictions apply to such substitutes?
  - What are the costs and benefits and advantages and disadvantages of such substitutes?

The Agencies would have the public believe that it's analysis of the impact of deca-BDE is superior to that of international, Federal and other state organization's with substantially better fiscal and scientific resources.

Yes, we note the derivate analysis that deca degrades into other products that may be more toxic as the sole basis for this recommendation. If this was truly a major concern, with reliable scientific backing, then is it reasonable that other governments would not have acted on this concept to limit the use of deca-BDE. They have not.

The evidence on degradation is tenuous at best. The Agencies analysis focuses on the worst possible case extrapolated from limited scientific evidence. Evidence that is contradicted by other well designed work such as these examples:

- Scientific evidence, by Jacob de Boer, a Dutch environmental scientist, that as Deca-BDE in the environment increases, the components of penta are decreasing. This is evidence based on actual environmental finding in the Scheldt river, and should be most important when considered against laboratory data and speculation.
- Ikonomu also published a paper indicating that deca-BDE in a Canadian river was not responsible for the penta found in the same river.
- Laboratory study, by Cornelius Zetsch, a noted German UV degradation scientist, shows that deca-BDE could degrade, upon exposure to ultraviolet light, by very slowly losing bromine, but that the degradation would proceed sequentially, Br 10 to Br 9, etc., all the way to Br 0, therefore passing through penta, but not stopping. His study therefore concludes that all bromination levels, 9,8,7,6, etc. should be found, in the environment, not just penta/tetra. This is not the case.
- Zetsch also showed that the actual isomers of penta found in the environment ( the location of the bromines on the diphenyl ether substructure) would be different that those that are produced by photolytic degradation of Deca. He concludes that it is extremely unlikely that Deca is responsible for the components of penta in the environment.
- Deca does not degrade under the conditions for anaerobic degradation as verified by a Swedish study.

(note: full text of studies are being provided via other commenters)

**Recommendation:** Washington state should conform to the standards being developed by the United State Environmental Protection Agency for the management of any of the version of PBDE.

- The EPA is already taking action on octa and penta BDE. As quoted in the draft CAP. "EPA is in the process of developing a Significant New Use Rule (SNUR) for Penta- and Octa-BDE. The rule would require notification to EPA prior to manufacture or import of Penta- or Octa-BDE for any use

- after January 1, 2005.177 EPA's authority to issue SNUR's comes from The Toxic Substances Control Act section 5(a)."
- The USEPA is studying deca-BDE to determine if any action is warranted. Per the presentation provide by USEPA nothing has thus far indicated that any action is necessary. Hence, Washington state should take no action other than to monitor on-going research and agency actions.



#### Attachment 4

**Precautionary Principle.** This concept has been around since the cave man in one form or another. When a real danger can be identified it is better to take some early actions to increase “public” safety. The challenge these days is the threats are subtle and can create fear without having a basis in science. Look at the current definition of Precautionary Principle:

**Principle 15 (the *Precautionary Principle*) from The Rio Declaration on Environment and Development (1992), reads:** *Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation.*

**Interpretation found in literature:** *Where there is reasonable certainty of a cause-and-effect relationship resulting in significant harm from a specific, well-defined activity, absolute proof should not be required to initiate cost-effective remedial action.*

Thus we have a chemical such as deca-BDE which has not been shown in itself to be a hazard to human health in anything close to the dosage that have been observed; or are even likely to occur. Yes, it accumulates, but with a half life of 12 days in human body can not be considered persistent. Nor, has any study found it to be toxic except vague concerns about neurological damage in high dosages in experimental animals. Data poorly translated to humans without much more work. So, lacking a real threat ( “threats of serious or irreversible damage”) on which to base a claim for deca-BDE restrictions, ban proponents attempt to create a derivative problem by asserting that the breakdown products may create another threat. Please note the phrase- “lack of full scientific certainty” in the definition. Full certainty may not be required, but; some certainty is needed that there is really a threat of serious or irreversible damage. The degradation derivative concept is so scientifically uncertain, as discussed in attachment 3, as to fail even approaching the Rio international standard. The EU may have put a good point on this topic in the response to Ecology: EU staff responded:

“The Conclusion is that further information and testing are required in an attempt to demonstrate whether the substance is or is not a safe product.”

Hence, the resources of the EU, the godfather of the Precautionary Principle, is unable to find adequate reason to determine a product is unsafe, including consideration of its derivative products. This raises the question of the standards of certainty under which the Agencies are making their recommendations.

The WDOE continues to lose credibility with reasonable people when it takes actions that are so clearly outside the rational boundary of the precautionary principle. These actions risk the Agencies losing further credibility in the application of this principle in any situation. As described in Governor Locke’s blue ribbon report the WDOE already has a unsatisfactory reputation with the

State's regulated community- private and public. This is another action that reinforces that image and will encourage an increased logjam of legal, legislative and public opposition to WDOE actions- good and bad. Such logjams in Agencies activities will adversely affect the protection of the natural and the business environment.

Recommendation: The Agencies should drop the proposed ban on deca-BDE. Instead, consider a proposal to monitoring the science as it develops from the many agencies currently investigating deca-BDE. Should sufficient scientific information surface identifying a realistic problem, then the department can propose actions with-in the frame work of the (under development) PBT rule. The Agencies may wish to look at deca-BDE as though it were subjected to the reviews of a significant new rule by including risk and impact analysis.

Attachement 5.

**Social, Safety and Economic Impacts.**

Comment: The proposed recommendations on the PBDE's have multiple social, safety and economic impacts that have require extensive additional study. A few of the areas needing attention are:

- **Recycling:** Two sets of recommendations are needed to differentiate between the impact of Octa/Penta-BDE ban and Deca-BDE. The Octa/Penta-BDE issue will quickly become one of recycling and reuse since the supply of these products will end about July 2005. Hence, the question becomes do we accept products that are manufactured from recycled content that may have some level of Octa/Penta-BDE. A strict ban on new products containing these materials would necessarily require that any new product be certified to not have Penta/Octa-BDE recycled content. The recyclers have testified that they have no knowledge of what is in the products they get. Hence, they would of necessity reject everything that could- maybe- have Octa/Penta-BDE in them. So what happens to these products? They end up in land fills, along side roads, dumped on charities and the problem just becomes exacerbated in other area. Eventually, these products end up in landfills- probably safe locations considering current landfill standards; but at what cost to the environment in use of virgin materials instead of recycled products. For example; as recommended "new" products made from recycled materials, such as the plastic "2x4" could not be sold in Washington. Instead we would need to use virgin materials such as forest products or imported oil to make the alternative products. California passed an inclusive Octa/Penta ban, then came back and amended the law to address a range of recycling issues they had not adequately considered. Washington State should learn from California's experience and carefully craft rules on recycling and new products containing recycled content to maximize environmental benefits.
- **Manufacturing buy-back:** In a related concern is the WDOE's proposal to create a "manufacture buy-back" requirement. The topic has been hotly debated at NEPSI meeting held under USEPA auspices. It is also the topic of consideration in a WDOE solid waste advisory group created by legislation in 2004 session. All reference to this approach for management of any material- PBDE or otherwise should be stricken from this CAP pending legislative resolution of the surrounding policy issues.
- **Consumer Electronic deca-ban:** The proposed ban on deca-BDE in electronic equipment is both inappropriate as discussed above and likely to cause far more harm than good. The category of materials covered in this proposed ban is equivalent to those in the EU ROHS listing. That is just about every electrical and electronic item from basic components such

as wire and transistors (sold to hobbyists) to after-market car components. The deca-ban would affect not only average consumers, but; also small and large businesses that use a range products covered under this definition. Boeing uses thousands of office products ordered from suppliers such as Office-Max, Boise.com and others.

Even if a ban were imposed it is problematic if it is going to be effective in reducing public exposure to deca-BDE. Look at Ecology's own figures on PBDE availability in table 7 of CAP- as expressed as reflection of waste stream: (note: this appears to be all PBDE, not just deca-BDE). Notice that electronics is .3% (.003) of the waste steam! The department needs to demonstrate how eliminating .3 percent of the products from the waste stream, and by implication available products in consumers home, can have any realistic impact on public health. Especially when:

- The Agencies own data suggests that the majority of exposure to PBDE's is through food consumption.
- Food production in the US is so sophisticate that much of it comes from a few central locations (CA, FL, Midwest); hence,
- A majority of food consumed by Washington residents is likely from out of state.
- Thus the proposed ban on PBDE's in electronics is going to have minimal effect on body burden caused by eating food; the alleged major source.

Only an effective Federal ban on a product can create a business environment in which a deca-BDE ban on electronics would be effective. The Montreal Protocol and related EPA action is an example where this can work. However, such a ban is not likely in the foreseeable future as the US EPA does not see a need at this time to ban or restrict the use of deca-BDE (see earlier discussion).

- **Fire Codes:** Boeing also has concerns about fire safety should deca-BDE be unavailable in our offices and factory electronics. The National Fire code has many requirements for flammability standards in the work place that have been adopted by local ordinance. It is entirely feasible that some parts of these codes could not be satisfied with available substitutes.

Concern for our employees safety is a central ternate of our operations; both at work and home. We have appended several articles from the European press addressing fire safety issues. It is particularly interesting to note that while there are about the same number of fires per-year the number of deaths in Europe is nearly 4 times higher

"The estimated impact of fires in each continent is listed in Table 1. The financial cost of fires is exceptionally high. Direct property losses **amount to 0.2% of total GDP and the total cost of fire to society has been calculated at 1% of GDP.** Protection of life and property from the effects of fire has been a topic of a great deal of research, much of which has focused around prevention of the spread of

flame using barriers and flame retardants. To recognize how these materials work, you have to understand the burn process.

Continent	Population (millions)	Fires per year (millions)	Fire deaths per year (thousands)
<b>Europe</b>	<b>720</b>	<b>2.2</b>	<b>25.0</b>
Asia	3660	1.0	30.0
<b>North America</b>	<b>470</b>	<b>2.3</b>	<b>6.5</b>
South America	340	0.5	2.5
Africa	780	0.8	5.0
Australia	30	0.1	0.3
TOTAL	6000	6.9	69.3

[citation: **Melting in the heat.(International Pages)(Statistical Data Included)** HARDING, PAUL; CROMPTON, GEOFFREY Asia Pacific Coatings Journal, v13, n4, p16 August, 2000 ]

In the CAP is a discussion of the purpose of flame retardants that can be summarized as: Giving the occupants more time to escape prior to flashover. In a impact analysis the Agencies could advise the public if they are four times as likely to die in a fire due to removal of effective flame retardants- such as deca-BDE; An impact analysis seriously missing in this plan.

**Recommendation:** The Agencies need to conduct a suitable risk and impact analysis prior to making its recommendations. All recommendations that affect usage of deca-BDE as a flame retardant should be withdrawn until the analysis are completed, reviewed and publicly commented on.

## Attachment 6

### **Exemptions and waivers:**

**Comment:** Washington DOE needs to ensure that an exemption or waiver process is incorporated in any scheme to manage PBDEs. These options are needed to ensure these products can be used when unique applications are required. As a parallel example, the Montreal Protocol on ozone depleters contains specific exemptions for uses such as Space Shuttle and waivers for uses for which there are no substitutes, such as foam blowing in certain missiles. The EU even recognizes this need as they have recently granted a interim waiver for use of Penta-BDE in aircraft escape slides- as there is not alternative available at this time.

- As a follow-up to the July QMI where there was lengthy discussion about the use of pentaBDE in certain escape slides, a meeting was held in Brussels to review the use and make a determination on possible derogation. The DRAFT COMMISSION DIRECTIVE, amending Council Directive 76/769/EEC with respect to restrictions on the marketing and use of pentabromodiphenyl ether in aircraft emergency evacuation systems for the purpose of adapting its Annex: .
- "3. By way of derogation, until 31 March 2006 paragraphs 1 and 2 shall not apply to aircraft emergency evacuation systems."

**Recommendation:** The Chemical Action Plan should include a discussion of exemptions and waivers processes. These processes should not require the applicant to provide excessive documentation or research data. Rather, they should use the data currently at hand in making determinations. Waivers & exemptions granted by other governments should be de-facto sufficient reason to grant a waiver or exemption in Washington State.

Gale Group Trade & Industry DB

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14187015 SUPPLIER NUMBER: 81299682 (THIS IS THE FULL TEXT)

**Let's not lose sight of first principles. (Compounding).(Brief Article)**

British Plastics & Rubber, 28(2)

Nov, 2001

TEXT:

There is an old proverb about swamps and alligators which demonstrates that no matter what adversity one faces, it is important to keep one's mind on the job in hand. The chemistry surrounding the polymer industry is constantly being attacked for its negative aspects while the overwhelming benefits it may bring are overlooked. **Flame retardant chemicals get a lot of bad press, particularly halogenated materials. But as Anne Noonan of Great Lakes Polymer Additives reminds us, they also do a pretty good job of stopping people being burned to death.**

WHEN politics drives the debate over additives, the discussion often boils down to the call for a ban on all fire-retardant chemicals, starting with halogenated compounds. However, that position is increasingly at odds, not just with trends in the marketplace, but also with recent scientific findings and the resulting adjustments in official attitudes.

When science drives the issue the conclusions are very different. One global trend that is gathering pace is using science to confirm the key reason for using FR polymer additive technology in the first place -- namely, that these products save lives and property.

A look at developments in a number of countries reveals the strength of this trend.

**Sweden: Sweden has been generally credited with being most strongly against FR additives, with its Chemical Inspectorate providing the leading critical voice. Yet, in April 2001, the Chemical Inspectorate criticised as 'inconclusive' research by environmental activists in their case against brominated FRs. 'Just because a fire retardant contains bromine doesn't make it dangerous,' said Eva Ljung of the Chemical Inspectorate in remarks published in the April 26 issue of Miljorapporten, an environmental advocacy magazine.**

Of course, the Nordic countries are still looking closely and critically at FR products. In the past year, they've raised important questions about antimony, phosphate, and bromine-based FRs. But, again, the prevailing view highlights the role of these products in saving lives and property as the prime considerations.

The European Union: In Brussels, the European Commission and Parliament spent much time and many resources this year looking at brominated FRs in the context of the Waste Electrical and Electronic Equipment (WEEE) and hazardous substance ban (RoHS) directives. At one point, the Commission considered banning all brominated FRs. Instead, the Parliament passed a law that will ban rarely-used PBBs and PBDEs for electrical and electronic equipment.

Risk assessments are underway on two important FR additives -- decabrom and octabrom; scientific data generated to date proves that these chemicals are environmentally acceptable.

Japan: In Tokyo, the Japan Environment Association has recently changed its ecolabel criteria for copiers, printers, and PCs. The change withdraws the exclusion of all BrFRs to just PBBs and PBDEs, products that have little impact on the marketplace. Pressure for this change has filtered up from Japanese OEMs, who recognize the superior recyclability of BrFR plastics and also the consumer demand for greater fire safety.

United States: In recent years, the National Academy of Sciences examined the effects on human health of 16 FR chemicals used to meet new furniture fire safety standards. The studies produced enough data for the Academy to definitively evaluate eight of these products -- and it concluded that there were no significant environmental or health concerns related to their use.

Public safety factors

**The second major component of FR growth is the increased interest in improving public safety.**

**The US Consumer Product Safety Commission, the US Fire Administration, and the National Fire Protection Association issue annual estimates on fire losses in the nation. Based on these figures, it's estimated that there are approximately 400,000 residential fires each year requiring a response from firefighters. These fires kill about 4,000 people, with another 20,000 people suffering serious injuries from burns. The fires also result in property losses totalling about \$4.5 billion. Of these fires, approximately 70,000 involve electrical distribution and appliances; another 40,000 stem from fires in upholstered furniture and mattresses.**

**Perhaps the most interesting aspect about these statistics is that they grossly underreport the problem. For example, a congressional investigation revealed that the federal government, which employs two million civilians housed in 8,300 buildings, has no data on even the largest of fires on its own property. Also, and incredibly, there have been years in which large states such as California and Pennsylvania have not reported a single fire. Clearly, this shows that nationwide fire reporting systems are severely inadequate.**

**In Europe, the system for collecting and reporting fire data is not much better, but even with partial data, the member states of the European Union report about 80,000 people are seriously injured in European fires each year. Of these, some 60,000 are hurt in their homes.**

**One subset of fires that has attracted attention is the number of European fires involving television sets. According to the Swedish National Testing and Research Institute, about 160 people die each year in Europe as a direct result of TV fires. In Sweden, for example, which has relatively lax fire-safety standards for the plastic housings of TV sets, there are 165 TV set fires per million population. By comparison, the United States, with stringent FR standards in this area, shows less than two TV fires per million in population.**

**For all the criticism of FRs -- not by the scientists or even the environmentalists, but mainly by politicians -- the European Commission acknowledges there would be 20 per cent more European fire deaths if FRs were not being used. In the same vein, the UK reports that 1,860 lives have been saved in the past decade because of its safety standards for upholstered furniture, due to the use of FRs.**

Higher demand, greater safety

The marketplace is reflecting this need to deal aggressively with the massive destruction and cost of fires. Companies in turn are responding with products that use FR additives for extra safety in a vast array of Recent additions to the Great Lakes portfolio of flame retardants for thermoplastics are an intumescent additive for polypropylene and a high bromine content general purpose flame retardant for colour-sensitive compounds.

Reogard 1000 is a phosphorus nitrogen-based intumescent flame retardant that is melt blendable at PP's processing temperature and is said to increase the heat distortion temperature of the compound. It is also



non-blooming, has good electrical properties, and has a reduced tendency to absorb water.

PP containing Reogard 1000 is recommended for use in V0 PP homopolymers and low polyethylene content co-polymers. It can also be used in a number of impact modified grades.

The new Firemaster 2100 is a non-diphenyl oxide based brominated flame retardant supplied as a uniform white powder suitable for formulations requiring white or light coloured products.

Applications foreseen include television cabinets, foam insulation and wire and cable.

[www.pa.greatlakes.com](http://www.pa.greatlakes.com)

Factfinders:

Reogard 1000 122

Firemaster 2100 123

products, including highly combustible plastic outer casings and housings, candles, power cords, and the like.

In the United States, for example, televisions are made with fire-resistant outer housings. In Japan, some of the most prominent TV makers -- Panasonic, Toshiba, and Mitsubishi -- are now following suit. No regulatory agency or governmental power is making them do it. They just want to do the right thing.

This is another prevailing tendency that has recently emerged, what can be called the 'social conscience' trend. Companies are increasingly taking it upon themselves to improve the fire performance of their goods for marketing concerns, surely, but also to a greater extent for ethical reasons. Again, it's being done because it is the right thing to do.

There have been many 'Green Label' attacks on FRs over the years, but the untold story is that many ecolabels are increasingly reflecting the concerns that imposing restrictions on FRs may be creating increased risk of fire. In short, ecolabels often follow a common sense approach in their considerations of FR additives. As a result, more lives will be saved.

For instance, TCO, Sweden's ecolabel for computers, is expected to include fire safety standards in its next set of criteria. Why? **Fire safety officials from Sweden, Finland, France, the UK, Belgium, Germany, Canada, and the United States are worried about TCO's restrictions on FRs as a public safety question. Fire safety advocacy groups worldwide are urging TCO to include effective fire safety standards to help ensure that lives are not lost. Not just in Sweden, but governments worldwide are in greater agreement than ever before: fire safety and environmental concerns must be treated with equal importance.**

Product trends

The trends in upholstered furniture, appliances, and automobiles reflect significant increases in the use of FRs. Manufacturers are likewise responding with an array of new FR products and technologies.

Furniture: The US Consumer Product Safety Commission recently agreed to move forward with tough, new fire safety standards for mattresses. In July, California issued its own laws for improved safety of mattresses and bedding. In addition, a US consortium of companies and associations is now drafting federal legislation for higher safety levels for upholstered furniture, sleep products, candles, and cigarettes.

Appliances: The U.S. Underwriters Laboratory has just adopted new fire safety standards that will result in a significant increase in the use of FR chemical additives. More than 40 other UL standards, governing thousands of products, are directly affected, including hair dryers, toasters, power drills, and electric can openers. Manufacturers will have two choices: re-engineer their products or use fire-resistant outer

housings. The early indication is that most manufacturers view FR additives as by far the more cost-effective approach.

Automotive: The US National Highway Transportation Safety Administration plans to change its rear-impact test for cars from 30 to 50 MPH. The implications for fire safety are enormous, as it will affect how fuel systems, interiors, and even some exterior parts are made.

Manufacturers respond

Increasingly, additives manufacturers are heeding the call of the marketplace for improved FR additives that meet customers' exact specifications. This call has been prompted by recent scientific data on the efficacy of such materials as well as a heightened desire for greater public safety.

Manufacturers of FR products are following more sensitive environmental practices. By doing so there will ultimately be far less reluctance by manufacturers to employ FR technology to meet the overwhelming desire for greater fire safety in consumer products.

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**Flame Retardants.(flame retardents industry)**

Wigotsky, Victor

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**TEXT:**

Comparative photos show the dramatic fire-resistant effect of adding a small amount of nonhalogen Flamestab NOR116 retardant and synergist to the fibers of polypropylene cloth. Thirty-five seconds after flame removal, the test sample without the new additive burns intensely, while the protected material remains intact. Ciba Specialty Chemicals Corp.

The threatened bans on halogen flame retardants have not materialized in North America. These old standbys are holding their own, and new developments and market entries reflect a growing accepted technology. Still, the nonhalogens are making inroads in selected areas, although their cost and performance have not kept pace with those of the more efficient halogen products. In **Europe\*\*\*\*\***, however, the story is different. The nonhalogen flame retardants are thriving, and the halogen-based additives are under increasing restrictions because of environmental perceptions.

**Geographical differences**

"The market for flame retardants is growing at an annual rate of 4% to 6%," says Russ Kidder, executive vice president of the Fire Retardant Chemicals Association (FRCA). **"The Europeans\*\*\*\*\* are willing to settle for less fire safety rather than to use brominated flame retardants. This is seen most dramatically in television sets, which, for the most part, contain no flame retardant at all. As one might expect, TV fires\*\*\*\*\* have increased\*\*\*\*\* greatly since flame retardants have been eliminated from TV sets in Europe\*\*\*\*\*"** In the U.S., television sets and some unattended appliances, contain halogenated flame retardants; in these applications, fire safety is at high levels. In most appliances where nonhalogenated flame retardants are used, either the flammability rating or physical properties are below U.S. standards. Nonhalogenated flame retardants are receiving more research effort in the United States and have made some inroads in the market place. But cost/performance favors the halogenated products in many applications.

"There have not been many new regulatory standards for flame retardancy or fire safety promulgation in the last several years" Kidder continues. "Meanwhile, the California Bureau of Home Furnishings is trying to modernize and upgrade California Technical Bulletin 117 for upholstered furniture. This state activity should be complete in 2001. The mattress industry, on the other hand, is cooperating with the regulatory groups to upgrade the present mattress standard. Research work is being completed at the National Institute of Standards and Technology (NIST) and a proposed mattress fire safety standard should be issued soon. One major problem with the mattress standard is, how do you factor in the contribution of sheets and blankets to the fire safety of mattresses? Activities in other markets are at the early stages of development. Plenum wire and cable is one of these that could affect the use of flame-retardant chemicals."

**Phosphorus-based**

Akzo Nobel's Phosphorus Chemicals introduced Fyrolflex BDP (bisphenol A diphenyl phosphate) as the next generation nonhalogenated flame retardant for engineered resins such as PC/ABS and PPO/HIPS blends. Another major product is resorcinol-based Fyrolflex RDP.

Demand for bisphosphate nonhalogenated flame retardants continues to grow, especially in areas where environmental concerns are the strongest, says Ted Halchak, marketing and sales manager, The Americas. Capacity expansion and continued development of phosphorus-based approaches demonstrate Akzo's commitment to the future growth of nonhalogen-based products.

Fyrol PNX is an all-phosphorus, nonhalogenated flame retardant added to flexible polyurethane foam; one targeted area is in low-fogging automotive interiors. High efficiency permits reduced use levels. Fyrol CLP, containing chlorine and phosphorus, is being evaluated where flame-retarded flexible polyurethane foams are used.

The company expanded capacity of Fyrol PCF and Fyrol CEF, major flame retardants used in rigid polyurethane foams. The trend toward hydrocarbon blowing agents in place of fluorocarbons to comply with the Montreal Protocol has resulted in the incorporation of additional flame retardant to meet flammability standards. Volume expansion in the first quarter of 2001 will increase the availability of Fyrol FR2 and Fyrol 38, products used in the flexible polyurethane foam market. In the recent past, the growth rate of flame retardants in the flexible foam market has been just above GNP rates. Akzo Nobel's Phosflex flame-retardant plasticizers for flexible vinyl applications experienced moderate growth during the 1990s. A family of materials introduced a few years ago, the Phosflex 300 series, continues to make inroads through improved cost/performance.

#### Expanded line

Albemarle Corp. has been developing, acquiring, or forming alliances with other companies to expand its line with additional brominated products and new halogen-free technologies, such as phosphorus-based and zinc borate-based flame retardants. NcendX P-30 is phosphorus-based for PC/ABS, PPO/HIPS, and other polymers; Albemarle's first entry with halogen-free products, it is a clear liquid that improves the melt flow of the host resin. NcendX B-1000, UV, chemically, and thermally stable to 290(degrees)C, is another new halogen-free offering; it is zinc-borate-based and used as a flame retardant, smoke and afterglow suppressant, and anti-arcing agent. Available in **Europe\*\*\*\*\***, it is the product of a commercial agreement between Albemarle and The Borax Polymer Additives Group. Zinc borates have been used primarily in PVC, polyamide, and epoxy potting compound applications. Albemarle sees opportunities, however, in styrenics, engineering plastics, and other resins that take advantage of the low toxicity and flame-retardant performance of zinc borates.

Saytex CP-2000 (tetrabromobisphenol-A) is a highly pure reactive or additive flame retardant containing stable aromatic bromine and is produced in the world's first continuous process. As a reactive flame retardant, it finds application in epoxy and polycarbonate polymers and helps circuit boards achieve higher thermal stability and longer-term reliability than with nonhalogen additives. Tetrabromobisphenol A epoxy oligomer made with CP-2000 is widely used as an additive in styrenic polymers and many engineering thermoplastics, because the oligomer offers improved polymer viscosity and UV resistance.

Saytex HP-900 flame retardant is another of Albemarle's new bromine-based products. A high-purity grade of hexabromocyclododecane containing a high amount of aliphatic bromine, HP-900 allows reduced loadings. Its low melting point enhances melt processability, resulting in minimal effects on the mechanical properties of formulated systems. The flame retardant also has high solubility in common solvents, and offers potential to achieve transparent formulations. It can be used without the

addition of antimony oxide, primarily in extruded polystyrene or suspension-polymerized polystyrene foam. With a stabilization package and proper processing conditions, however, it is also usable in polystyrene and polypropylene resins.

Albemarle's Pyro-Chek 68PB, a brominated polystyrene additive for flame retarding a range of polymeric systems, features excellent thermal stability, moldability, and dispersibility. Because it is polymeric, it prevents migration and blooming in compounded resins. The company offers its own line of brominated polystyrene flame retardants as Saytex HP-7010. Saytex 8010 flame retardant responds to the increasing demand for recyclable polymer additives. Thermal stability and recyclability facilitate use in high-performance styrenic polymers, engineering resins, wire & cable, and elastomers. Outside analysis of samples demonstrated that resin compounds containing Saytex 8010 conformed to the German Dioxin Ordinance regulating dioxin and furan contents. Its chemical structure was developed to minimize the formation of brominated dioxins or furans during plastic processing, recycling, or incineration.

Most efficient

"Although there have been many reports, studies, and detailed looks at the overall health, safety, and environmental impact around the world on bromine flame retardants, to date there are no legislated bans or restrictions on the use of any of the commercially available bromine flame retardants," says Glade Squires, vice president, marketing, AmeriBrom, Inc. "The use of bromine flame retardants in all applications has been shown to be the most efficient and cost effective means of providing fire safety." The National Association of State Fire Marshals (NASFM) has publicly supported the use of bromine flame retardants in order to have the proper degree of fire safety built into goods. As a result, the use of bromine flame retardants continues to grow on a global basis.

Currently, the U.S. is poised to legislate the use of flame-retardant furnishings in all homes. The U.S. is behind other developed nations in requiring the use of flame-retardant home furnishings, Squires adds. So far, only California has had legislation covering flame-retardant standards for home furnishings sold in that state. California's fire statistics before and after the legislation testify to the need for this legislation nationwide.

As preparation was under way to draft legislation for furniture flammability standards on a nationwide basis, the Consumer Product Safety Commission (CPSC) enlisted the National Academy of Sciences (NAS) to make recommendations on the overall safety of flame retardants that would find their way into home furnishings. The final report from NAS, after it reviewed the requested data on these flame retardants, supported the complete and unrestricted use of both decabromodiphenyl ether and hexabromocyclododecane (two of the largest volume bromine flame retardants sold globally) in home furnishings.

Squires acknowledges substantial interest among OEMs in eventually incorporating nonhalogen FRs in their goods. "To date, however, there have been many nonhalogen FR products tested, and none has the overall efficiency and cost effectiveness of bromine flame retardants. Maintaining physical properties, particularly of thermoplastics, while achieving flame retardancy, is always the major challenge." Bromine flame retardants have been able to meet this challenge, Squires continues, based on the efficiency of bromine and the resulting low load levels needed to achieve the desired degree of flame retardancy. In the case of nonhalogen FR systems, the high load levels needed for these to perform severely affect physical properties and substantially increase the cost of final

formulations. "Also, the overall environmental impact of many of these nonhalogen FRs remains to be determined, since they have not been as thoroughly investigated and tested as bromine FRs." Nevertheless, to broaden its product portfolio, the Dead Sea Bromine Group (DSBG), a leading producer of magnesium hydroxide, also develops and sell nonhalogen flame retardants.

AmeriBrom's new products include FR-370, a bromine-containing phosphate ester that provides outstanding performance, light stability, and physical properties in polypropylene; and FR-372, an analog of FR-370 designed to meet the needs and demands of polypropylene fiber. FR-720, the 2,3 dibromopropyl ether of tetrabromobisphenol-A, used in polypropylene, provides expanded FR solutions for polypropylene by complementing the FR-370 in the product line.

FR-20 magnesium hydroxide is the Dead Sea Bromine Group's first nonhalogen flame retardant. Although not new, several unique surface treatments have grown sales significantly, particularly in TPOs. FR-6120 melamine cyanurate is DSBG's newest flame retardant. Although not new as a flame retardant to the industry, it provides more FR options for customers.

#### Effective retardant/synergist

Ciba Flamestab NOR116 is a new nonhalogen flame retardant and synergist for polyolefins. As a NORHALS, it also acts as a light stabilizer. It is effective at low concentrations and exhibits polymer compatibility and excellent extraction resistance. Since it is melt processable, it is less likely to diminish the functional performance of the host material. In addition, significant synergies can be realized when it is used with some traditional flame retardants, and the improved performance of these systems allows passing of some of the more stringent industrial standard flame-retardancy tests. Also, reduction in the level of conventional flame retardants can avoid detrimentally affecting light stability and mechanical properties.

Flame retardance results from the NFPA 701 and MVSS 302 burn tests on polypropylene knitted socks, without any flame retardant, show test failures, based on char length and after-flame criteria. The material, however, passed the tests with addition to the fibers of as little as a 0.5% concentration of Flamestab NOR116. Moreover, with the addition of NOR116 at levels as low as 0.25% in combination with brominated flame retardant, the polypropylene material passed the tests, allowing reduction of the halogen material by more than 50%.

Flamestab NOR116 can also be used as a synergist with traditional FR products in molded polypropylene.

#### Thermal stability

Great Lakes Chemical Corp. has developed three new products, Firemaster PBS-64, PBS-64HW, and CP-44B, out of its brominated styrene-based technology. Because of lower inherent hydrolyzable bromide content, they possess excellent thermal stability. Molecular weight is controlled to provide melt blendable, low melt viscosity polymers that improve the melt flow of filled and unfilled polyamides and polyesters. Firemaster CP-44B, a copolymer of brominated styrene and glycidyl methacrylate, has improved compatibility in polyamides and polyesters, helping reduce the amount of FR synergist needed.

The planned phase-out of lead-based solders in connectors and printed circuit boards will significantly increase the operating temperatures of the flame-retardant polymers. Flame retardants must not significantly reduce the heat resistance of their polymer hosts. The products show little effect on the HDT of the host polymer. Similar challenges are facing the manufacturers of printed circuit boards in

formulating for higher-temperature solder baths, whether based on tetrabromobisphenol A or the newer halogen-free systems.

Pressure has continued on the brominated **diphenyl ether** ( **PBDE** ) flame retardants in Europe. EU risk assessment on these products is nearing completion. Keith Hughes, Great Lakes' senior global marketing manager, flame retardants, says it is expected that DecaBDE and OctaBDE will be shown to not pose unreasonable risks to health and the environment. However, it is expected that risk reduction measures will be imposed in Europe on the use of PentaBDE. Great Lakes has developed new flame-retardant technology, Firemaster BZ-54, based on tetrabromobenzoate esters, as an alternative. A low-viscosity liquid, it contains 54% bromine and can replace pentabromodiphenyl-oxide-based flame-retardant systems in flexible polyurethanes and other applications.

Great Lakes has also introduced two new non-halogen systems mainly directed at PC/ABS and PPO/HIPS polymers. Reofos BAPP and Reofos 507 complement the existing Reofos TPP and Reofos RDP. Reofos BAPP, bisphenol A diphosphate, has excellent cost/performance and reduced tendency to migrate. Reofos 507, a proprietary monophosphate, is an alternative to BAPP in formulating low migration, hydrolysis-resistant PC/ABS compositions.

**Debate in Sweden and Germany examines whether perceived environmental issues associated with PBDEs, and flame retardants in general, outweigh their benefits in improving fire safety. A recent Swedish research program demonstrated that the use of flame retardants can actually reduce rather than increase environmental pollutants such as dioxins, dibenzofurans, and polyaromatic hydrocarbons. The two-year study, conducted by the SP (Swedish National Testing and Research Institute) in collaboration with IVL (Swedish Environmental Research Institute), consisted of an extended life cycle analysis comparing a television set manufactured to U.S. standards of fire performance (UL 94V0) with a comparable European model with a typically HB-rated cabinet. It included U.S. and European TV set fire statistics and full-scale room burns, and investigated recycling, incineration, and landfill options at end of life. The analysis indicated that emissions of key environmental pollutants (such as dibenzodioxins and polyaromatic hydrocarbons) were lower for the TV cabinet containing DecaBDE and antimony trioxide than for a non-flame-retarded HB cabinet. It is estimated that 160 people will die and 2000 will be injured each year in Europe as a result of fires in TVs.**

Hughes says that as fabricators and compounders try to improve the efficiency and safety of their operations, many are looking to more formulated products that may offer multifunctional performance, improved handling, and reduced material usage. Great Lakes has introduced two new 100% active FR masterbatches. Fyrebloc 100 and 101 are 70% antimony oxide in a polybromostyrene binder. The nondusting masterbatches can be used in a variety of polyamide and thermoplastic polyester applications. The company also has introduced a briquette form of tribromophenol, PH73-FF, which has much improved flow and anti-caking tendencies over standard tribromophenol.

The National Association of State Fire Marshals, pressing for improved fire performance in upholstered furniture, petitioned the Consumer Products Safety Commission (CPSC) in 1993 to consider a possible flammability standard. In 2000, the National Research Council of the National Academy of Sciences (NAS) completed its assessment of the use of flame retardants for CPSC in its Toxicological Risks of Selected Flame Retardant Chemicals. The report concluded that eight of sixteen retardants that were evaluated pose little or no health risk. The way is now open for

the CPSC to consider a small flame test ignition standard for upholstered furniture in the U.S. Meanwhile, an increasing number of the major U.S. furniture retailers have been voluntarily adopting the California CAL 117 furniture flammability standard for polyurethane foam used in furniture sold in the U.S. The Sleep Products Safety Council (SPSC) is working with the CPSC and NIST on the problem of mattress fires with the aim of developing an improved standard. These initiatives, if adopted, should lead to safer furniture and mattresses in the U.S. and an increased market for flame retardants in polyurethane foams and back-coating of fabric.

#### Broader supply

Harwick Standard is now supplying a full line of flame retardants to the thermoplastic industry--as it has in the past to the elastomer industry--says David R. Schultz, senior technical service representative. The company is a full-service distributor that supplies traditional flame-retardant systems that contain antimony oxide and halogens as well as halogen-free materials. The company has most recently aligned itself with Aluchem, a supplier of alumina trihydrate. Harwick Standard also distributes a range of products that permit a variety of compounding options.

#### Antimony trioxide

Oxychem is now the leading producer of antimony trioxide in the U.S., after acquiring the Fireshield line of antimony oxide from Laurel Industries and then more recently acquiring the Thermoguard line of antimony oxide from Atochem. Besides antimony trioxide, Oxychem produces the flame retardants Dechlorane Plus, Pyronil 45, and sodium antimonate. An aqueous dispersion of Dechlorane Plus and Fireshield H (antimony oxide) is now available from Oxychem, called Dechlorane Plus AD; this material is 67% active, containing a 3:1 ratio of Dechlorane Plus and Fireshield H. Dechlorane Plus can be used as a flame retardant in nylons and epoxies using several different synergists to obtain a UL 94 rating. These synergists include different zinc compounds and also iron compounds. By using these different synergists, one can obtain higher CTI values, improved thermal stability on processing, and lower cost formulation.

#### Flame-retardant masterbatches

PMC Group Polymer Products provides new offerings within its standard and custom Endura flame-retardant masterbatches and has acquired the North American Avantara ignition-resistant HIPS product line from BASF Corp. Early in 2000, the company finished matching its masterbatches to many of the common resin grades, defining loadings that give UL 94V-2 and V-0 ratings, and measured the associated physical properties. Compounders can use the database to shorten time to commercialization of new flame-retardant compounds.

Polymer Products can provide in developmental quantities a highly loaded melamine cyanurate concentrate for unreinforced nylon and polyester, says business manager Don G. Barber, "that eliminates direct-addition processing difficulties and allows the compounder to produce a lower-cost nonhalogen system." Also, available in developmental quantities is a new masterbatch for PC/ABS. In addition, two cost-effective masterbatches designed for the construction film market, Endura PE-101 and PE-102, have recently been commercialized.

#### Non-lead PVC

PolyOne Wire & Cable says the company sees continued growth in non-lead PVC products. In response to this projected market need, PolyOne has new wet-rated, non-lead compounds for THHN-2 and THWN-2 applications slated for commercialization this year. Demand is also steadily growing for the company's LSFOH (low smoke zero halogen) products introduced into the



U.S. in 2000. While demand for flame-retardant PVC compounds will remain high, PolyOne expects to see continued growth for these materials in specialty contract work sectors such as mass transit, tunnels, airports, and nuclear reactors. The company's ECCOH (Enviro-Care zero-halogen) compounds remain an option for jacketing applications that must meet these requirements. PolyOne supplies standard and custom grades of polyvinyl chloride (PVC) insulation and jacketing materials for a wide range of cable applications, including riser, plenum, and low-acid gas PVC cable.

#### Plenum cable

The growth of computer and communication networks has greatly increased use of plenum spaces for cabling, says Donald G. Ouellette, industry manager, Vinyl Division, Teknor Apex Co. As one generation of computer and communications technology succeeds another, new cable runs are necessary to accommodate the changes. A typical generation of plenum cable lasts three to five years before replacement. More often than not, installers leave the old cable in place and run the new cable alongside or on top of it, **increasing** the **fire** load within the enclosed space. And because plenums facilitate the movement of air within buildings, the fire performance requirements for cables installed there are especially stringent. Teknor Apex developed its PVC-based Fireguard line of low-flame, low-smoke compounds because of the high levels of flame resistance and smoke suppression required in plenums. Ouellette says the company diversified the Fireguard program by developing a series of nonhalogenated Fireguard LSZH (low-smoke, zero-halogen) compounds. "While U.S. standards bodies place their greatest emphasis on compounds that pass the most stringent flame test," he comments, "their counterparts in **Europe** currently emphasize compounds that mitigate or remove the perceived potential for halogenated cables to generate excessive amounts of smoke and irritating or corrosive gases during a fire. Our Fireguard LSZH compounds are selling very well," Ouellette continues, "but not for cable to be installed in the U.S. Most companies that purchase LSZH compounds use them for cables to be installed in **Europe**. In the U.S., where fire safety standards for communications cable are more stringent, there is no strong opposition to halogenated materials like PVC."

**The European market for data and communications cable is dominated by nonhalogenated compounds consisting of polyolefin resin (typically polyethylene or its major copolymers) and such flame retardants as aluminum trihydrate and magnesium hydroxide. These materials pass the JEC 60332 test for riser cable, which is the most stringent fire test mandated in Europe, but not the NFPA plenum-cable test. In effect, there is no plenum cable standard in Europe. In addition, the standard riser-cable test specified in the U.S., based on UL 1666, is more stringent than that in JEC 60332. "Several of our Fireguard LSZH compounds can pass both riser tests," says Ouellette.**

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**Flame retardants-a cause for debate.**

AUTHOR: Tyler, A.

JOURNAL: Performance Chemicals Int., (Performance Chemicals International (PCI)), Volume 14, Issue 2, Page(s) 5

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**ABSTRACT: A report from the University of Surrey on the risks and benefits of flame retardants has boosted the case for brominated flame retardants. Risks and benefits in the use of flame retardants in consumer products was commissioned by the UK Department of Trade and Industry. It indicates that the risk of death or injury from a fire involving consumer products can be reduced by 30-90% by using flame retardants.** A European Union risk assessment of polybrominated diphenyl ether flame retardants is scheduled for publication in summer 1999. Environmental groups in a number of European countries have claimed that there are significant potential risks to human health and the environment linked to the use of flame retardants.

DESCRIPTORS: flame retardants ; risk assessment ;

CHEMICAL SUBSTANCE(S): polybrominated biphenyl ethers

SECTION: Precautions (12)

SECTION CROSS-REFERENCE: Hazardous Waste Management (02 )

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**TESTING/STANDARDS: Forum Attacks Sweden Food Toxin Article.**

Flame Retardancy News, v9, n12, pNA

Dec 19, 1999

TEXT:

An Oct. 11 article in Sweden's daily newspaper, Dagens Nyheter, entitled "Environmental Toxin Discovered In Food," inaccurately described tetrabromodiphenylether as a flame retardant, according to Bromine Science and Environmental Forum chair Michael Spiegelstein (BSEF, 118 Ave. de Cortenbergh, 1000 Brussels, Belgium; Tel: 32-2 733 93 70, Fax: 32-2 735 60 63). TeBDE is not a flame retardant used in consumer electronics, says Spiegelstein. TeBDE is called a flame retardant in the article, because it has been used as a minor part of one flame retardant application for other uses, he says.

A possible explanation for the occurrence of TeBDE in the Baltic is its previous use in bell-bore fluids by the oil industry in the North Sea, and for several years in hydraulic fluid used by the mining industry in Northern Europe. All of the use was stopped several years ago, because those using the substance realized how emissive it was.

One of the studies of polybrominated diphenyl ethers (PBDEs) presented at the Dioxin '99 conference recently held in Venice, Italy indicates that the levels of PBDEs in the environment actually are leveling off and in certain cases even diminishing. The logical conclusion of this is that the levels that can be found in the food chain in all probability also will soon drop, asserts Spiegelstein.

If levels in the environment continue falling, as is expected, says Spiegelstein, it is a confirmation that the probable source is the earlier use in the oil and mining industries, and that it has no connection with flame retardants. Blaming every finding of TeBDE on flame retardants is not only factually incorrect-it also causes unnecessary concern about flame retardants, he says. **Flame retardants are not used frivolously in many consumer products. On the contrary, they can mean the difference between survival and death in a fire. After the use of brominated flame retardants in television sets was stopped in Sweden, television fires increased by 100%, he points out.**

BSEF agrees with the authors of the article that TeBDE in the food chain is a serious issue, Spiegelstein says. But, he adds, to automatically blame flame retardant use without investigating other possible explanations risks the existence of such flame retardants on a lack of a scientific base. A balanced scientific approach must be taken-it must not be forgotten that brominated flame retardants save lives in potential fire situations every day, he urges.

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**Melting in the heat.(International Pages)(Statistical Data Included)**

HARDING, PAUL; CROMPTON, GEOFFREY

Asia Pacific Coatings Journal, v13, n4, p16

August, 2000

**TEXT:**

Many conventional fire retardants are reduced in effectiveness at elevated temperatures when a fire is at its most dangerous. Special ceramics cause the paint to melt and then fuse to form a permanent, impervious glaze. Fire costs millions of dollars and hundreds of lives every year. Although Asia has a small number of fires in proportion to the population size, the fires can cause much more damage and a higher loss of life. The estimated impact of fires in each continent is listed in Table 1. The financial cost of fires is exceptionally high. Direct property losses **amount to 0.2% of total GDP and the total cost of fire to society has been calculated at 1% of GDP.** Protection of life and property from the effects of fire has been a topic of a great deal of research, much of which has focussed around prevention of the spread of flame using barriers and flame retardants. To recognise how these materials work, you have to understand the burn process.

Continent	Population (millions)	Fires per year (millions)	Fire deaths per year (thousands)
<b>Europe</b>	<b>720</b>	<b>2.2</b>	<b>25.0</b>
Asia	3660	1.0	30.0
<b>North America</b>	<b>470</b>	<b>2.3</b>	<b>6.5</b>
South America	340	0.5	2.5
Africa	780	0.8	5.0
Australia	30	0.1	0.3
TOTAL	6000	6.9	69.3

Average per year		
	Fires per 1000 people	Fire deaths per 1000 fires
<b>Europe</b>	<b>3.1</b>	<b>11.4</b>
Asia	0.3	30.0
<b>North America</b>	<b>4.9</b>	<b>2.8</b>
South America	1.5	5.0
Africa	1.0	6.3
Australia	3.2	3.0
TOTAL	1.2	10.0

**Table 1: distribution of fires by continent (Courtesy of the Centre of Fire Statistics of CTIF)**

The development of a fire is a cyclic phenomenon. From a small ignition source, enough heat is released to create an initial fire. This initial fire can then increase the ambient temperature to the point at which repeat ignition occurs, leading to fire growth, releasing more heat and combustion side products, including partially oxidised flammable gases. The next stage is where most of the remaining material erupts into flames. This flashover generates a developed, mature fire that quickly becomes difficult to contain. The

mature fire may burn through containing walls, propagating the flame to adjacent areas and leading to re-ignition, starting the cycle. Flame retardants block the growth of flame. The common methods of retarding the flame include:

- \* halogenated systems: halogenated materials, such as antimony trioxide or pentoxide, chlorinated paraffin and other brominated materials, are considered to be effective flame retardants. There is, however, mounting concern about the toxicity of the gases generated in large quantities during the combustion of halogen-containing polymers. Despite their efficiency, there is growing demand for halogenated systems to be banned and substituted with non-halogenated systems

- \* non-halogenated systems: the majority of non-halogenated flame retardants produce water vapour or carbon dioxide at elevated temperature to stifle a flame. Typical non-halogenated flame retardants include alumina trihydrate  $\text{Al}(\text{OH})_3$  (or ATH), huntite  $\text{MgCa}((\text{CO}_3))_2$ , and magnesium hydroxide  $\text{Mg}(\text{OH})_2$ . These materials are effective in stifling a burn at low temperatures and over an extended period of time. However, both methods stop acting at elevated temperatures. When a fire is at its most dangerous, and once the extinguishing agent has been exhausted, they often provide a source of fuel for a flame.

At higher temperatures, a greater defence is needed. Materials, such as zinc borate, can help create a glassy char and slow heat flow through the host material. The chars formed by these materials block heat flow and suppress afterglow once a burn has stopped but are brittle and often fall off a substrate, revealing more fresh surface to burn, reducing the host material's integrity. Finally, there is a material type that is active at higher temperatures. It slows or stops entirely the emission of smoke and toxic fumes, forms a stable glassy char to limit heat flow and retains host integrity. This material is called 'Ceepree' and is composed of a mixture of glass-like and ceramic-like materials known as flits. Rather than relying on chemical emission degradation, Ceepree works by melting as the temperature increases. The secret to the success of this material lies in its ingredients.

Conventional glass flits, similar to window glass, begin to melt at about 650 (degrees) C and pass through melt, flow and fusion as a steady transition with increasing temperature. Figure 1 shows the behaviour of three frits when heated. The graph represents the typical area of a sample viewed from the side using a thermodilatometer. A conventional frit would undergo the following stages during a melt:

(Figure 1 ILLUSTRATION OMITTED)

- \* softening: the material begins to melt; the volume has not yet changed significantly (up to 600 (degrees) C in Figure 1)

- \* sphere: the volume of the frit reduces considerably as the melt progresses and the voids between particles disappear. (600-800 (degrees) C in Figure 1)

- \* half-sphere: the melt is underway, the volume continues to reduce as the cohesion of the sample pellet is lost entirely. (800-1100 (degrees) C in Figure 1)

- \* fluid: the frit is now a liquid. As a fire barrier material, a conventional flit would run and drip off the substrate at this point (above 1000 (degrees) C in Figure 1)

To counteract this final stage, Ceepree contains a devitrifying frit that crystallises and sets hard prior to final melt and fusion. Figure 2 shows the action of a devitrifying flit under temperature, softening at 800 (degrees) C, melting and flowing to 950 (degrees) C

at which point it crystallises (devitrifies) and remains in that hard state to 1200 (degrees) C before melting and flowing again to fuse at 1300 (degrees) C.

(Figure 2 ILLUSTRATION OMITTED)

A material that did not begin to protect until a fire was already established and mature would not be useful so, to enable earlier activation of the material, Ceepree often contains a soft frit or one activated at a lower temperature. Figure 3 shows the melt of a typical soft frit occurring at approximately 450 (degrees)C.

(Figure 3 ILLUSTRATION OMITTED)

Combining these materials (Figure 4) gives a product that activates at the same temperature as low melt frits but devitrifies when the soft frit begins to flow and stays in this crystalline state to 900 (degrees) C. It flows and fuses between 900 and 1100 (degrees) C. This final flow and fuse, when used in a flammable carrier material, binds the char together and protects substrates by promoting formation of an insulating layer of glass and carbonaceous char.

By adding components, it is possible to modify the behaviour of a Ceepree frit combination to include some intumescence before and during the devitrification stage. The intumescence (foaming) provides more protection to the host material by providing a hard shelled foam of cells filled with carbonaceous char. Formation of this carbonaceous foam results in a significant increase in volume of the material as shown in Figure 4.

(Figure 4 ILLUSTRATION OMITTED)

#### HOW CEEPREE WORKS

The action and changes in the Ceepree material can be demonstrated by using the simplest grade of Ceepree, 'C200', as an example. \* below 350 (degrees) C: Ceepree is an inert component in the host material. (Figure 5)

\* 350-400 (degrees) C: when heated below its activation temperature of around 350-400 (degrees) C (the soft frit melt point), the low melt components within the Ceepree formulation begin to melt, causing vitreous material to flow over and around the burning host material and beginning to form a char. The picture (Figure 6) shows Ceepree after the melt. The continuous surface forms an effective barrier to fire and smoke. The melt and flow process is endothermic and absorbs the heat from the flame. The char helps to disperse and absorb heat from the flame. The encapsulation of the host also inhibits the access of oxygen to the combustible materials, preventing carbonaceous and volatile decomposition products from being emitted as smoke.

\* 750-800 (degrees) C: the devitrifying component of the Ceepree begins to act, passing from a glassy to a crystalline state and remaining in place, maintaining host material integrity and adhering the char to the surface of the host material.

\* 1200 (degrees) C: the Ceepree is still continuing to act, retaining its integrity and protecting the host material.

Typical activation profiles for Ceepree frit combinations are shown in Figure 7.

This type of fire barrier solution has a number of uses, from paint to plastics, caulks, mastics and structural panels, and it can save lives.

Ceepree-based systems are effective in small, enclosed areas or where there is potential for a mature flame to spread. It prevents the emission of toxic fumes, and can provide valuable escape time. The formation of a continuous surface to starve the flame and the action of

the char in absorbing heat can also provide time for the fire to be fought. Ceepree-based paints have been used in US Navy submarines, where the suppression of smoke and flame is vital and in multi-story apartments where the potential for the spread of a mature flame from one apartment to another is extremely high. Ceepree-based systems can also be used over existing solvent based paints or onto bare or primed wood.

#### RECENT DEVELOPMENTS

Ceepree has evolved significantly since it was patented 12 years ago. Despite its advantages, it was limited in application because of some limitations:

- \* Water solubility: some elements of the frit mixture were initially chosen for their partial water solubility, making Ceepree unsuitable for exterior application. An insoluble mixture of frits has now been formulated for paints, plastics, cable and exposed areas.

- \* pH of the flit combination: Ceepree in its simplest form is alkaline and can cause stability problems and setting in many acrylic resin systems. The solution to this problem was simple but had evaded many paint formulators. Small amounts of boric acid (itself a fire barrier material) counteract the alkalinity of the Ceepree, and stable grades are now available for use in water-based media.

- \* particle size: Ceepree was originally only manufactured with a median particle size of 30um. This prohibited its use in paints requiring thin film application, many powder coatings and extruded thermoplastics. Two finer grades of Ceepree - 'Microfine', with a (d.sub.50) of 5(micro)m, and 'Ultrafine', also with a (d.sub.50) of 5(micro)m but with the coarse tail removed, show promise in thermoplastic cabling and powder coatings. The finer particle sizes give Ceepree Microfine and Ultra fine grades a higher surface area and form the continuous surface more readily.

- \* high activation temperatures: the original Ceepree frit combination did not become active until 450(degrees)C, at which point the fire was already burning freely. Ceepree Products is currently working on the commercialisation of two patented grades with lower activation temperatures.

Ceepree materials have one other great advantage. Their action is a physical change of state rather than a chemical process so they are compatible with all known fire retardant systems and can be used in conjunction with them.

In many cases, the flame retardant will act synergistically with the Ceepree, lowering the activation of the soft frit and slowing the melt process, providing better encapsulation of the host material. Although the action of Ceepree-based systems is simple, the relationships with other fire barriers and flame retardants can be complex. Ceepree Products offers a high level of technical support to help users to reach an economically viable protection from flames.

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